Control of the wetting properties of ^{4}He crystals in superfluid

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To investigate whether it is possible to control the wetting of ^{4}He crystals on a wall in superfluid, the contact angles of ^{4}He crystals were measured on rough and smooth walls at very low temperatures. A rough wall was prepared in a simple manner in which a commercially available coating agent for car mirrors, which makes the glass surface superhydrophobic, was used to coat a glass plate. The contact angles of ^{4}He crystals were increased by approximately 10° on the rough wall coated with the agent. Therefore, the increase in the repellency of ^{4}He crystals in superfluid was demonstrated to be possible on a very rough surface. The enhancement of the contact angles and a scanning electron microscopy image of the coated surface both suggest that a Cassie-Baxter state of ^{4}He crystals was realized on the surface; the crystals did not have full contact with the wall, but entrapped superfluid was present beneath the crystals in the hollow parts of the rough wall.

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I. INTRODUCTION

Controlling the wetting of liquids on a wall has significance in both fundamental science and practical engineering [1]; however, control of wetting of a quantum crystal in superfluid ^{4}He has not yet been achieved. Superfluid ^{4}He is known to completely wet almost all solid walls when it coexists with its vapor phase [2]. This is because attractive interactions between ^{4}He atoms are much weaker than those between ^{4}He atoms and the solid wall. This causes a well-known superfluid phenomenon of film flow, where superfluid ^{4}He climbs out of a container and drops from its bottom [3]. When superfluid ^{4}He coexists with the crystal phase, however, it only partially wets the wall with a finite contact angle [4,5]. This is because the wall-crystal interfacial energy α_{wc} is comparable to and slightly larger than the wall-liquid interfacial energy α_{wl}. One might wonder why the crystal simply does not wet a wall completely, since the crystal has higher density than the liquid. It is usually believed that the stress field close to the wall is important to increase the wall-crystal interfacial energy and causes partial wetting. The only known material that shows complete wetting or epitaxial growth of hexagonal-closed-packed (hcp) ^{4}He crystal is graphite [6].

The equilibrium contact angle θ of a ^{4}He crystal in superfluid on a wall obeys the Young equation,

$$\cos\theta = \frac{\alpha_{\mathrm{wl}} - \alpha_{\mathrm{wc}}}{\alpha_{\mathrm{lc}}}, \tag{1}$$

as if it were a fluid, because the relaxation of the ^{4}He quantum crystal to an equilibrium state that minimizes the interfacial energy is very quick at low temperatures. Here, α_{lc} is the superfluid-crystal interfacial energy, and the anisotropy of the crystal is neglected. It has been reported that $\theta \approx 135°$ for ^{4}He crystal on various types of solid wall [6,7].

In general, crystallization and melting are inevitably accompanied by mass and heat transport processes, which are limiting processes for a first-order phase transition of ordinary classical matter. In the case of ^{4}He, however, the mass is transported swiftly by superfluid, and the latent heat is negligibly small due to the small entropy difference between the crystal phase and the quantum condensed superfluid phase at low temperatures. Therefore, these transport processes are not the limiting process for crystallization, and the mobility of the crystal-superfluid interface is determined by the collision of elementary excitations onto the interface. The number of excitations becomes smaller at lower temperatures and thus the mobility becomes divergently higher toward $T = 0$ K. This allows one to observe a very quick relaxation of ^{4}He crystals and their equilibrium contact angles at low enough temperatures.

In the case of classical fluids, the roughness of a wall assists repulsion and alters the contact angle, which is referred to as the lotus effect [8,9]. Superhydrophobic or superoleophobic surfaces have been realized on the textured surface of a wall [10–12]. The intriguing question is whether the lotus effect is possible for the ^{4}He quantum crystal in a superfluid. In the ^{4}He crystal-superfluid system, it is known that a couple of layers of high-density ^{4}He solid exists on a wall, attracted by the strong van der Waals potential. However, it is unclear how these solid layers affect the wetting of a ^{4}He crystal on a rough wall. There are also some arguments that superfluid layers exist between a ^{4}He crystal and the solid layers on a wall, when the wall is rough, even above the crystallization pressure of 25.3 bar [13–15]. It has not been clarified whether wall roughness would have an influence on the contact angle and enhance wall repellency toward the quantum crystal in a superfluid.

We have been observing the equilibrium crystal shape in zero gravity using the parabolic flight of a jet plane; however, the ^{4}He crystals have never detached from the wall, even in zero gravity, due to partial wetting onto the wall [16–18]. Therefore, we have attempted to float ^{4}He crystals in superfluid or to move the contact line pinned on the wall using acoustic radiation pressure [19–21]. If a wall can be made repellent

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to ^{4}He crystals and the contact angle can be controlled, then the zero-gravity experiment would become easier with much less perturbation to the system. We have attempted to slide a ^{4}He crystal on a transversely oscillated plate in a sawtooth fashion, utilizing the difference between static and dynamic friction [22]. If the contact angle is altered by roughening the plate surface, then the sliding motion would be influenced, which would allow the sliding motion to be investigated more systematically under a controlled boundary condition. We have also studied the collision of ^{4}He crystals against a wall in superfluid [20,23]. It is known that a liquid drop bounces on a superhydrophobic surface [10]. If a ^{4}He crystal bounces on a wall with high repellency as the liquid drop does, then it would pave the way to investigating a novel limit for the collision dynamics of a crystal to achieve crystallization and melting at an extremely high rate in superfluid. Therefore, control of the wetting properties of ^{4}He crystals in superfluid could lead to many opportunities for the investigation of dynamical phenomena related to walls. Here, we have attempted to change the contact angle to the wall by roughening the wall, and we investigated whether such control of the wetting is possible. A glass plate was coated with a commercially available coating agent for car mirrors, with which the car mirror becomes superhydrophobic and is kept dry even in heavy rain. The coating agent on the glass plate acted to repel a ^{4}He quantum crystal in superfluid at low temperature.

II. EXPERIMENT

A glass plate was coated with a coating agent (Glaco Mirror Coat Zero, Soft99 Co.) [24]. Although details regarding the coating agent's contents and its mechanism to repel water are not available, superhydrophobicity could be achieved both chemically and structurally with the coating agent. The surface of the coating material would consist of hydrophobic chemical groups, although it is not obvious whether these groups are effective to repel ^{4}He crystals. However, the coated surface of the glass would be structurally roughened to enhance the effective surface area and maximize the hydrophobicity of the surface. Therefore, the roughened surface structure should help to enhance the repellency of the glass plate toward ^{4}He crystals.

To coat the glass plate with the coating agent, the glass plate was first cleaned in acetone using an ultrasonic cleaner. After drying to remove acetone, the coating agent was sprayed onto the surface. Figures 1(a) and 1(b) show scanning electron microscope (SEM) images of the coated glass surface in different scales. For SEM imaging, the surface was coated with a thin Pt film, on the order of 5 nm, to avoid charging. Particles of the coating agent, a few tens of nm in size, were aggregated on the glass surface and formed a disordered rough surface. The disorder seemed to be multiscale and was extended over a wide range from tens up to several hundreds of nm. Figure 1(c) shows an SEM image of a control surface (bare glass plate) with a Pt film, which was much smoother than the coated surface.

For this experiment, a glass plate was used with one side coated and the other side uncoated. The glass plate was placed in a sample cell with optical windows to observe the

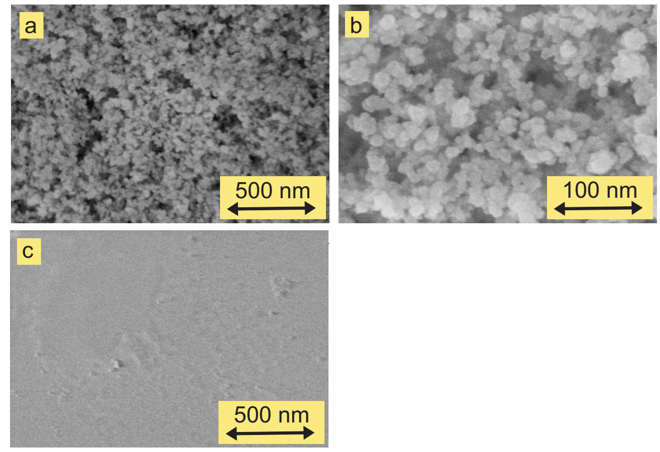

FIG. 1. (a) and (b) SEM images of a glass surface coated with a car mirror coating agent. The coating roughened the surface significantly on multiple scales. (c) SEM image of a control glass surface without the coating.

contact angle of ^{4}He crystals. Figure 2(a) shows the glass plate ($10 \times 10 \times 1.5$ mm^3) adhered to the upper part of the cell with its surface aligned parallel to the observation direction. An ultrasonic transducer was installed just above the glass plate and was used to nucleate a seed crystal.

A ^{3}He-^{4}He dilution refrigerator with optical windows for *in situ* observation of the ^{4}He crystals was used to cool the cell. This refrigerator was originally designed for use in a small jet plane for the zero gravity and ultralow temperature experiments. Details of the refrigerator have been reported elsewhere [16]. The observation windows were aligned in a straight line, and infrared filters were installed on the thermal shields at 70 and 4 K. The ^{4}He crystals were illuminated from the back window using a parallel light, and the contact angle was observed from the front window.

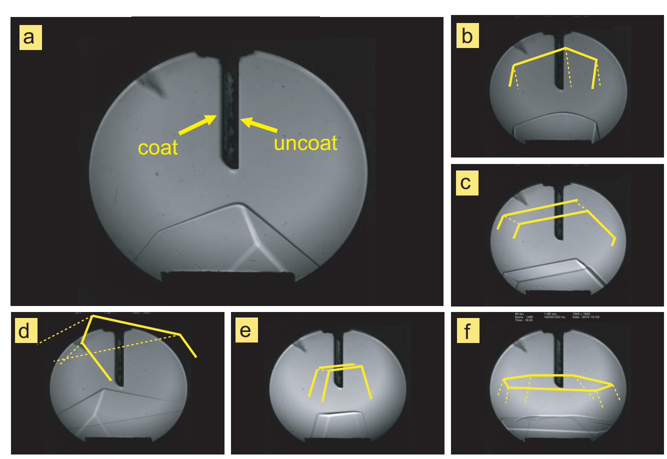

FIG. 2. (a) Overall view of the experimental cell through observation windows. A glass plate was attached vertically on the upper part of the cell and its surface was aligned in the observation direction. Coated and uncoated sides are indicated. Growth of a ^{4}He crystal with the hcp structure from the cell bottom and its *c* and *a* facets are clearly observed. (b)–(f) Typical growth of crystals with different orientations used for measurement of the contact angles. Profiles of the crystals are drawn in the upper part of each frame.

The experimental procedure was as follows. By condensing ^{4}He through a capillary at low temperature, superfluid ^{4}He filled the cell and was pressurized to slightly below the crystallization pressure. The pressure was then slowly increased to a few millibars above the crystallization pressure, and an ultrasound pulse was sent into the metastable superfluid to initiate nucleation of a seed crystal [20,23]. The seed crystal was enlarged on the ultrasonic transducer by the addition of ^{4}He, and then eventually fell in the superfluid and landed on the bottom of the cell. As the crystals fall, they change their orientation from time to time, which provided crystals with a wide variety of orientations. The seed crystal was grown on the bottom of the cell, as shown in Fig. 2(a); during growth, clear facets became observable in the growth shape, indicating that the crystals had different orientations, as shown in Figs. 2(a)–2(f). The single crystal eventually filled up the lower part of the cell. When the crystal-superfluid interface reached the glass plate, the addition of ^{4}He was stopped. The contact angles of the ^{4}He crystal on the coated and uncoated sides of the glass plate were simultaneously determined from the observation image. Although contact angles are known to change, depending on whether the interfaces are advancing or receding [6], the contact angle measurement was made under equilibrium conditions because it is the basic quantity that should be measured first. Although the advancing and the receding angles are also important, we have not measured them yet. The temperature range was between 0.48 and 1.45 K; ^{4}He crystals have hcp structure in this range.

III. RESULTS AND DISCUSSION

When a crystal-superfluid interface reached the glass plate, its contact line was lower from the horizontal interface level away from the glass plate due to partial wetting of the crystals. The menisci appeared in the vicinity of the glass plate, in the range of a capillary length l_c on the order of 1 mm [4,5], as shown by the typical example given in Fig. 3(a). Figure 3(b) shows a magnified view of the menisci, and the level of the contact line was lower on the coated surface side than on the uncoated side, which indicates the larger contact angle on the coated side. Contact angles were obtained for both sides of the glass plate from the magnified images using the fitting as follows. The profile of the interface was fitted by a function,

$$x - x_0 = l_c \cosh^{-1}\left(\frac{2l_c}{z}\right) - 2l_c\left(1 - \frac{z^2}{4l_c^2}\right)^{1/2}, \qquad (2)$$

where z and x are the height variation of the interface and the horizontal position [1]. The capillary length is expressed as $l_c = \sqrt{\alpha_{lc}/\Delta\rho g}$. Here, $\Delta\rho$ and g are the density difference between the solid and the liquid and the gravitational acceleration constant, respectively. The contact angles were obtained from the slope of the fitting function at the wall on both sides and plotted in Fig. 4. We have also tried to measure the contact angles visually on a computer screen by using protractor software, and we checked the consistency independently. The obtained overall behaviors were consistent with each other, and the scatter of the data was similar in both measurements.

The contact angles obtained from the fitting are plotted as a function of temperature in Fig. 4. Measurements were conducted for 12 crystals with different orientations, which are distinguished by the different symbols in Fig. 4. The orientation is not specified in Fig. 4, because no systematic dependence of the contact angles on orientation was recognized. Open symbols represent the contact angles θ for the uncoated surface side, while solid symbols represent those θ^* for the coated surface side. Figure 4 shows that θ^* are clearly larger than θ, although there were a few points where θ^* was smaller than θ. A total of 46 data points of contact angles were obtained in Fig. 4, and three data points of crystal no. 8 at around 1.4 K had the significant opposite dependence; a majority of the obtained data (about 40 out of 46) supported the repellency of crystals on the rough wall. Therefore, it is reasonable to draw a conclusion by taking an average that the coating agent on the glass plate acted to repel ^{4}He crystals in superfluid,

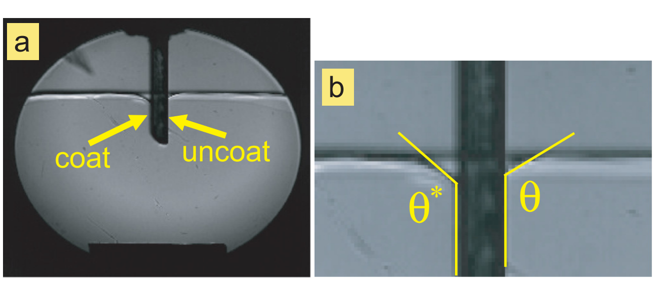

FIG. 3. (a) Horizontal crystal-superfluid interface touching the vertical glass plate. (b) Enlarged image of the contact region. The menisci of the crystal-superfluid interface appeared in the vicinity of the glass plate, where the contact line was lower on the coated left side than on the uncoated right side. The contact angle on the coated side θ^* was larger than that on the uncoated side, θ.

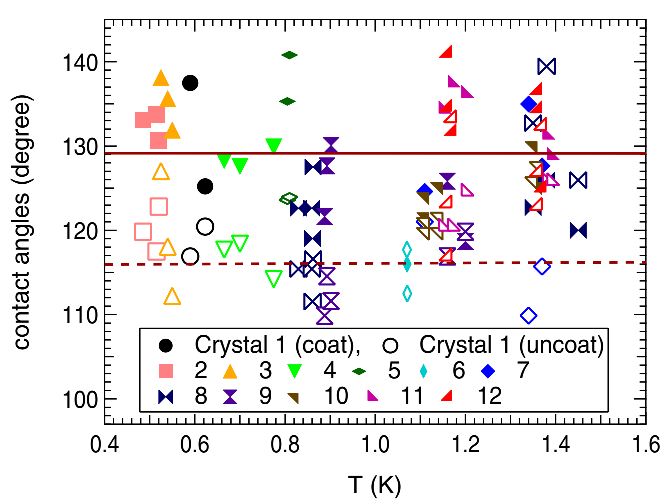

FIG. 4. Contact angles for ^{4}He crystals of different orientations as a function of temperature. Different symbols represent the different crystals. Closed symbols are the contact angles for the coated side θ^*, and open symbols are those for the uncoated side, θ. The solid and dashed lines represent the average for θ^* and θ, respectively. θ^* was larger than θ in most cases, which indicates that the coated surface successfully repelled the ^{4}He crystals in superfluid at very low temperatures.

even at very low temperatures. Average values of the contact angles were $\theta^* \approx 129^\circ$ and $\theta \approx 116^\circ$. The typical difference θ^*-θ was approximately 10°, and the largest difference was approximately 20°.

Crystal no. 8 showed the opposite dependence and was anomalous. The photo of crystal no. 8 is shown in Fig. 2(f) to specify the orientation. However, we have no clear explanation for the anomaly, and we do not explore it in depth in this paper.

One might think that the contact angles are not the same even when both sides are smooth as soon as the orientation of the wall is not a high-symmetry plane. Since most of the crystals of different orientations showed the enhancement of the contact angle on the rough wall, the enhancement was realized even when the orientation of the wall was far from a high-symmetry plane. This would mean that anisotropy of the surface energy was not large enough for rough surfaces of the ^{4}He crystal, which are largely tilted from the high-symmetry surface, to influence the enhancement of the contact angle. An intrinsic orientation dependence of the contact angle might exist for the vicinal surface with large anisotropy, but the measured crystals were not sufficiently aligned to resolve such a fine anisotropy effect.

Our average value for the uncoated smooth surface was $\theta \approx 116^\circ$. This is smaller than the usually reported value of 135°, even considering the relatively large scatter in our data. We have no clear answer for this systematic difference. One possibility is that the measured contact angles might have been specific to the used glass surface. At any rate, the contact angles were measured simultaneously on both coated and uncoated sides, and the enhancement of the repellency on the coated side can be regarded as a robust result.

For a liquid drop in air, the Wenzel state [25] and the Cassie-Baxter state [26] are known as states on a rough wall that exhibit higher repellency than on a flat wall. While a liquid drop partially wets the wall of a perfectly flat surface, a wall of the same material but with a moderate roughness repels the drop and achieves the Wenzel state, in which the liquid drop has full contact with the rough wall. In this configuration, the macroscopic flat surface area is smaller than the microscopic total surface area, and thus the contact angle is increased. A wall with more intense roughness, usually extended over a multilength scale, achieves the Cassie-Baxter state, in which the liquid drop is sustained on the protruding regions of the surface asperities, and air is trapped between the drop and the microscopic hollows. In this configuration, the macroscopic contact area of the drop to the wall includes the microscopic contacts with the wall and air, which makes the rough wall more repellent to the drop than the flat wall. When this mechanism is applied to a crystal-superfluid system of ^{4}He, the liquid drop and the air correspond to the crystal and the superfluid, respectively.

If the Wenzel state is realized in the ^{4}He crystal in the superfluid, the contact angle is altered as [25]

$$\cos\theta^* = r\cos\theta, \tag{3}$$

where $r = A_{\text{tot}}/A_0 > 1$ is the ratio between the microscopic total surface area of the wall, A_{tot}, and the macroscopic effective surface area, A_0. Using the averages $\theta^* \approx 129^\circ$ and $\theta \approx 116^\circ$, we obtain $r \approx 1.4$. Although it is difficult to accurately estimate r for the wall from Fig. 1, $r = 1.4$ seems to be too small to characterize the highly disordered surface. Therefore, the Wenzel state is not probable in the ^{4}He crystal in superfluid on the coated glass plate.

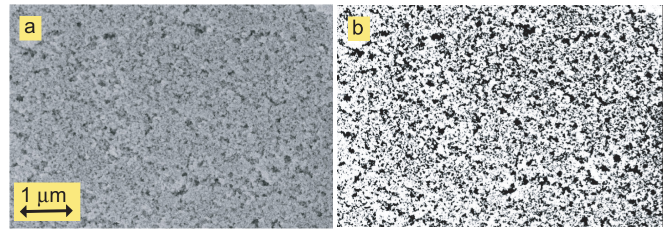

FIG. 5. (a) SEM image of the rough surface of the glass plate coated with a coating agent. (b) Binarized image with an appropriate threshold. The white part fraction was $\phi \approx 0.7$.

If the Cassie-Baxter state is realized in the ^{4}He crystal in superfluid, then the contact angle can be estimated from the equation [26]

$$\cos\theta^* = -1 + \phi(\cos\theta + 1), \tag{4}$$

where ϕ is the fraction of the area where the crystal actually has contact with the wall, and $1 - \phi$ is the fraction of the area where the superfluid liquid is trapped between the crystal and the hollow of the rough wall. We obtained $\phi \approx 0.66$ from the measured average values of θ and θ^*.

To evaluate whether this value of ϕ is reasonable, we attempted to extract the fraction of protruding regions of the coated wall from the SEM image. Assuming that the protruding regions appear as bright contrast and that the hollow regions appear dark, the SEM image of the coated wall in Fig. 5(a) was binarized using an appropriate threshold value to separate the protruding and the hollow regions, as shown in Fig. 5(b). The black regions indicate the hollow regions where the superfluid liquid is supposed to be entrapped between the crystal and the wall, while the white regions indicate the protruding regions where the crystal has microscopic contact with the wall. Although this analysis seems rather crude, an estimate of the roughness of the wall can be obtained. The fraction of the white parts was estimated to be $\phi \approx 0.7$ from Fig. 5(b), which is in approximate agreement with that obtained from Eq. (4). Therefore, in the case of a ^{4}He crystal in superfluid on a coated glass wall, the Cassie-Baxter state is most likely to be realized and induces the repellency of the quantum crystals.

It is an intriguing problem whether the ^{4}He crystal really has direct contact with the wall at the protruding regions in the Cassie-Baxter state, as in the liquid drop case, or if a thin superfluid film exists between the crystal and the protruding regions. If there is always a thin superfluid film both on a flat wall and on a rough wall with the coating, then the roughness would not significantly change the surface energy between the crystal and the wall, and it would have a minimal effect on the contact angle of the ^{4}He crystal. Our observation of the enhanced repellency of the ^{4}He crystal on the coated wall implies that the crystal has contact with the walls without a superfluid layer on the smooth wall and on the protruding regions on the rough wall, while liquid is trapped in the hollow region on the rough wall.

Although repellency of the ^{4}He crystal was achieved and the Cassie-Baxter state was realized, contact angles were not significantly altered by the use of the coating agent on the glass plate. This method was sufficiently simple to demonstrate clearly that control of the contact angle of ^{4}He crystals in superfluid is, in principle, possible. However, the lotus effect of ^{4}He quantum crystals with $\theta^* \approx 180^\circ$ was not achieved in the superfluid. It would therefore be worthwhile to prepare a more elaborate surface decorating structure, such as micrometer-scale high pillars, to achieve the lotus effect with ^{4}He crystals, as was demonstrated for liquid drops [10]. Vibration of the wall is known to help repel a liquid drop [27]; therefore, application of acoustic waves to the glass plate could also be a promising way to achieve the lotus effect.

Realization of the Cassie-Baxter state on a rough wall will provide some insights into other wall-related phenomena in the He system. In connection with the supersolid issue in ^{4}He, mass flow has been investigated in ^{4}He crystals and was reported to occur below 0.6 K and 28 bar [14,28–31]. The flow path can be either through the crystal or the superfluid layer between the crystal and the wall, and it is very important to distinguish between the two. Although no superfluid layer exists on a smooth glass surface [32], superfluid can survive in the hollows of a rough wall, as in the Cassie-Baxter state. Thus, a possible origin of the observed mass flow is via the superfluid on the rough parts of the wall. If the superfluid in hollows is connected, then mass could be carried at a distance. Cessation of the mass flow above 28 bar could thus be related to disconnection of the percolation path of the superfluid in the hollows between the crystal and the wall [14,28–30]. The growth and upward motion of a macroscopic superfluid droplet in a ^{4}He crystal was reported [5,33,34]. Mass flow is required for droplet growth, and the superfluid trapped on the wall would be able to act as a source of mass flow. In a field of superfluid ^{3}He, the use of very dirty walls has drawn attention as a means to achieve complete suppression of the order parameters on the wall [35,36], and the present demonstration of the rough wall will have implications for the preparation of such dirty walls.

IV. SUMMARY

To investigate whether control of the contact angle of a ^{4}He crystal in superfluid is possible, the contact angles of ^{4}He crystals with different orientations on a rough surface were measured. The rough surface was prepared by coating a glass plate surface with a commercially available coating agent used to impart superhydrophobicity. Contact angles on the coated rough surface θ^* and the uncoated smooth surface θ were measured simultaneously and compared. θ^* was determined to be larger than θ in most cases, and thus alteration of the contact angle was possible. From consideration of the contact angles and SEM images of the rough surface, the Cassie-Baxter state was determined to be the most likely state to be realized on the rough surface. The ^{4}He crystal has contact with the protruding parts of the rough surface, but superfluid is entrapped between the crystal and the hollow parts of the wall.

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